Photoinduced formation of ferromagnetic clusters in $La_{0.9}Ca_{0.1}MnO_3$ thin films

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Microwave losses due to conductivity and magnetic permeability are investigated in $La_{0.9}Ca_{0.1}MnO_3$ films illuminated with photons in the energy range of $E = 0.5 - 2$ eV. Growth of photoinduced ferromagnetic hysteresis is observed when the magnetic field is swept between -15 and 15 mT at temperatures below 60 K. The time required for saturation of the opening of the hysteresis loop depends on the photon energy having the minimum of ≈ 40 s at the illumination intensity $I = 3.5 \times 10^{14}$ photons/cm^{2}s. Both photoinduced magnetization and the increase of microwave photoconductivity can be well explained with a model assuming that small ferromagnetic regions exist within an insulating ferromagnetic phase of the sample and that these regions are expanded by optically induced charge transfer between Jahn-Teller split e_g states of neighboring Mn^{3+} ions.

I. INTRODUCTION

Following the discovery of a photoinduced phase transition from an insulating antiferromagnetic (AFM) to a metallic ferromagnetic (FM) phase in $Pr_{0.7}Ca_{0.3}MnO_3$,[1] several interesting papers have been devoted to this phenomenon in Pr based manganites.[2,3] An insulator-metal transition was observed by conductivity measurements in $Pr_{1-x}Ca_xMnO_3$ ($x = 0.3 - 0.5$) single crystals under optical excitation at photon energies between 0.6–3.5 eV using a combination of a Nd-YAG pulse laser and an optical parametric oscillator.[1,2] In thin $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films the AFM/FM phase transition was observed by magnetization measurements at low temperatures under illumination with a He-Ne or an Ar laser[3] using the light flux density of five orders of magnitude lower than in Refs. 1 and 2. The illumination time required for the transition from the AFM to the FM phase was a few hours. An insulator-metal transition has been found in $Pr_{1-x}(Ca, Sr)_xMnO_3$ ($x = 0.3 - 0.5$) compounds also under low temperature x-ray irradiation.[4–6] These photoinduced effects are attributed to formation of metallic FM clusters within the AFM phase under optical excitation, but the mechanism of the process is not clear.

Charge, orbital, and spin ordering play an important role in electrical and magnetic properties of manganese perovskites and lead to phase segregation at temperatures well below the Curie temperature T_c. Recent theoretical investigations predict an electronic phase separation of the FM state into FM insulating and FM metallic phases.[7–9] ^{55}Mn NMR investigations provide experimental evidence for existence of these two phases.[10] The phase separation phenomenon is sensitive to the doping level (x), the temperature, and the magnetic field,[7–10] and also should be sensitive to illumination. The effect of the light could be related to optical excitation of additional carriers what is equivalent to an increase of x.

In this paper we present results of the investigation of photoinduced change of the ferromagnetic hysteresis detected at low temperatures by microwave absorption in thin $La_{1-x}Ca_xMnO_3$ (LCMO) films with $x = 0.1$. An unusual nonexponential time dependence of the magnetization and microwave conductivity signals observed after turning on the light is analyzed within the model of charge transfer optical excitation between Mn^{3+} ions localized in the FM regions of different phases.

II. EXPERIMENT

The experiments were made on films deposited on $NdGaO_3(100)$ substrates with a XeCl laser ($\lambda = 308$ nm) at the pulse power density of 2 J/cm^2. The substrate temperature was 700 °C and the oxygen pressure in the deposition chamber was 0.25 torr. The powder for the deposition target was made from a stoichiometric mixture of high purity La_2CO_3, $CaCO_2$, and MnO_2 salts by calcining the mixture at first for 35 h in air at 1320 °C and then for 22 h at 1375 °C, with intermittent grindings. Disk shaped films had the diameter of 3 mm and the thickness of 160 nm as determined from the edge of the films by atomic force microscopy. The thickness was selected so that the films were sufficiently transparent at the wavelengths of the light used in the experiments.

The magnetic properties of the samples were investigated by an rf-SQUID magnetometer. The temperature dependences of the magnetization of a ceramic pellet and films measured after a zero field cooling procedure at the magnetic field $B = 2$ mT are shown in Fig. 1(a). The ceramic material (curve 1) shows the phase transition from the paramagnetic (PM) to the ferromagnetic state at $T_c \approx 170$ K. A similar transition is observed for a film according to the phase diagram for the PM/FM transition in LCMO ($x = 0.1$).[11] The decrease of the magnetization in the temperature range below 70 K is
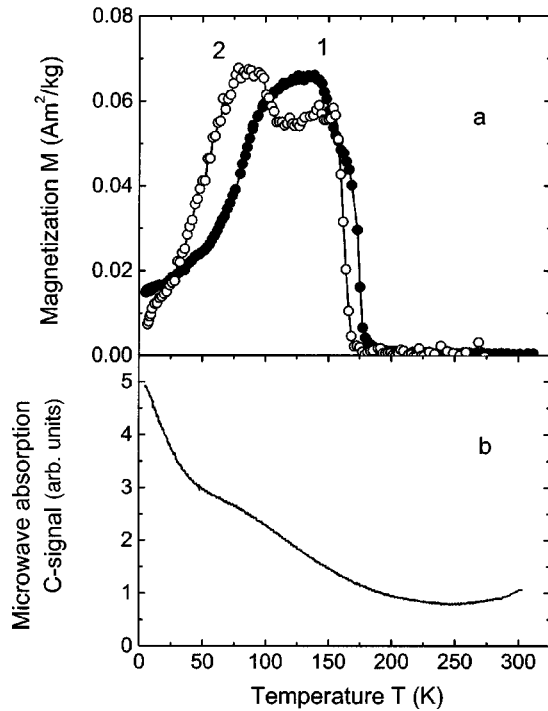
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FIG. 1. Temperature dependencies of the magnetic moment M for a ceramic (curve 1) and a thin film (curve 2) sample (a), and the microwave absorption C signal (see the text) for an unilluminated film (b) of LCMO($x=0.1$).

FIG. 2. Hysteresis of the microwave absorption M signal without illumination (A) and under illumination (B), measured at $T = 5$ and 15 K.

usually observed for low doped manganites and can be attributed to formation of other magnetic phases.[12]

Microwave absorption experiments were performed with an EPR spectrometer operating at the frequency of 9 GHz in the absorption mode and modified for sweeping the magnetic field **B** through zero value. The film was placed in the center of a cylindrical cavity at the position of the maximum microwave magnetic field $h_1 \perp B$. The surface of the film was parallel to **B** and inclined with an angle of $\theta \approx 20°$ from the direction of h_1. The sample was illuminated either with white light from a 100 W tungsten halogen lamp or by monochromatic light at wavelengths between 0.5–2.5 μm. The intensity of the light was measured by a bolometer. The temperature of the sample was varied between 3–300 K in a helium gas-flow cryostat.

In the geometry used the electrical component of the microwave field is not zero within the sample and increases with increase of the angle θ. The losses due to the absorption of this component of the microwave field by free carriers decrease the Q-factor of the cavity. The absorption of the electrical component is widely used for investigation of spin dependent microwave photoconductivity in semiconductors.[13] In the experiments with thin LCMO films we choose $\theta \approx 20°$ to optimize the illumination conditions and the amplitude of the detected signals.

We observed two types of signals. First, the dc voltage measured directly on the microwave diode, called the C signal, gives the amount of the microwave power reflected from the cavity. In thin films this signal has the main contribution from the microwave losses due to the conductivity of the sample.[14–16] The contribution of the dynamic magnetic permeability is much lower because of the small volume of the
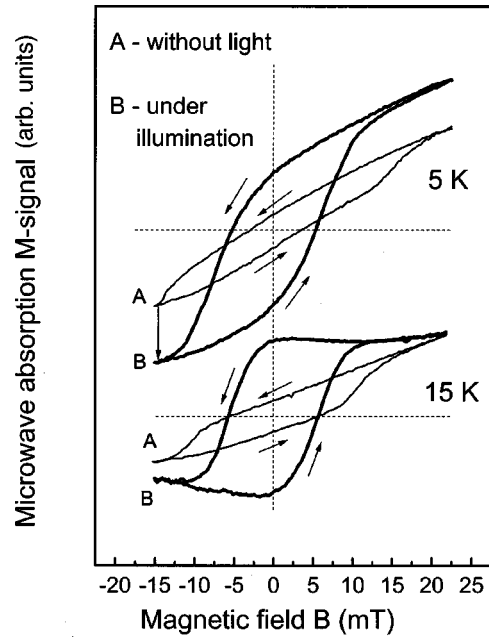
sample and the low amount of the magnetic Mn ions involved. This is confirmed by observing an increase in the C signal when θ is increased.

The second type of signals, the M signals, were observed using a lock-in amplifier and modulation of the magnetic field B at 100 kHz. In this case only the magnetic field dependent part of the microwave absorption is detected. Taking into account the high sensitivity provided by this technique both the field dependent part of the microwave conductivity and the magnetic permeability can be observed.[15,16]

III. EXPERIMENTAL RESULTS

The temperature dependence of the total microwave absorption (C signal) detected at $B=1$ mT in the LCMO ($x =0.1$) film without illumination is shown in Fig. 1(b). Increasing microwave absorption is observed below $T_c \approx 170$ K when the temperature is decreased. The increase of the microwave losses at $T<60$ K, due to growth of the microwave conductivity, is unusual for LCMO ($x=0.1$) which shows decreasing dc conductivity in this temperature region.[11] It should be noted that the dc and the microwave conductivity cannot coincide for the samples containing, e.g., conductive droplets in an insulating matrix.

Under illumination of the film by white light no significant changes were found in the temperature dependence of the C signal, except the decrease of the microwave losses at $T<60$ K due to heating of the sample by light. As estimated from the temperature shift of the curve shown in Fig. 1(b) the heating did not exceed 5 K under illumination with white light from the 100 W tungsten lamp. Instead, a weak increase of the C signal was found under illumination by monochromatic light. This increase will be discussed below.

As shown in Fig. 2(a) a strong photoinduced effect was observed in the hysteresis of the microwave absorption under modulation of the magnetic field (M signal), when scanning
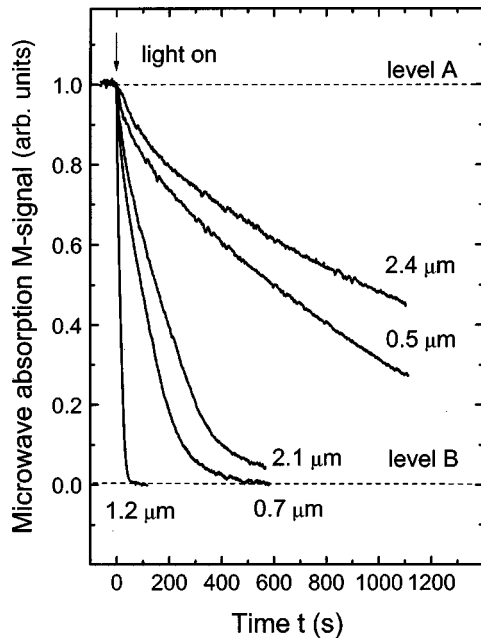
FIG. 3. Dependencies of the microwave absorption M signals on the illumination time at $B = -15$ mT and $T = 15$ K for different light wavelengths.
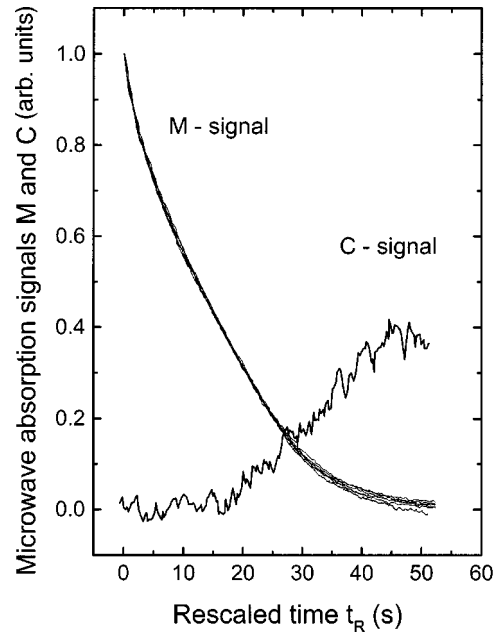

FIG. 4. Dependencies of the amplitudes of the M and C signals on the rescaled time $t_R = k(\lambda)$. The C signal is an average over 24 plots.

the field up and down within the range of $-15 - +25$ mT. When the sample is not illuminated (traces A) the hysteretic behavior of the absorption is weak. The slope of the hysteresis loop decreases when the temperature is increased. This slope originates from the zero-field absorption line usually detected in microwave absorption experiments.[15,16] Under illumination a strong hysteresis appears in the M signal (traces B). Measurements at different temperatures (see Fig. 2) clearly show that this effect cannot be explained by heating of the film by light.

The photoinduced hysteresis is observed in the range of temperatures 3 K$< T <60$ K. The amplitude of the hysteresis loop saturates at a very low light intensity but the time of the transition from the loop A to the loop B (see Fig. 2) in a fixed magnetic field decreases linearly when the intensity of the light is increased. This allows us to investigate the time dependence of the A-B transition under illumination with monochromatic light at different wavelengths λ and $B \approx -15$ mT. The results are shown in Fig. 3.

First, the time required for completion of the transition A-B depends on the wavelength. The shortest time, about 40 s, is observed for $\lambda = 1.2$ μm when the illumination intensity is $I \approx 3.5 \times 10^{14}$ photons/cm^{2}s. Second, the time dependencies are nonexponential and they cannot be described by a sum of two or more exponential components, either. However, all these curves coincide after rescaling the time axes by a factor $k(\lambda)$ which is related to the absorption of the light in the sample and depends on the wavelength. The rescaled plots of $M(t_R)$ with $t_R = k(\lambda)t$ are shown in Fig. 4. In the same figure is shown also the time dependence of the C signal detected under illumination without modulation of the magnetic field B. Because of the low signal to noise ratio for the C signal, the plot of $C(t_R)$ represents an average over 24 time dependencies observed at the values of λ given in Fig. 3. The increase of the C signal under illumination cannot be related to heating of the sample by light, because for T

<60 K the heating should decrease the microwave absorption signal according to Fig. 1(b).

The spectral dependence of the scaling factor $k(\lambda)$ in Fig. 5, obtained by normalization of the experimental data against the light intensity I at different λ, shows that the photoinduced microwave absorption efficiency has a maximum at the photon energy of ~ 1.2 eV.

After switching off the light the microwave absorption M signal does not change during a few hours at a fixed strength of the magnetic field. The initial hysteresis loop A (see Fig. 2) is achieved only after demagnetization of the film, increasing the magnetic field up to 50 mT and decreasing it again to -15 mT in dark. This behavior is similar to that
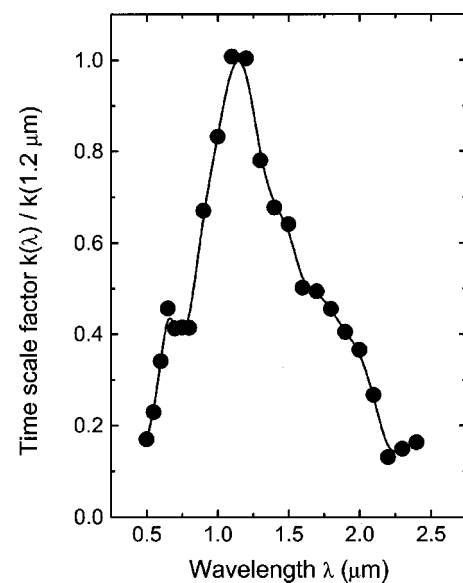

FIG. 5. Dependence of the time scaling factor $k(\lambda)$ on the wavelength.

observed in the $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ thin film.[3] We have detected hysteresis loops in unilluminated thin ferromagnetic Ni and Co films having the same shapes as the loops B. These results show that the light-induced magnetization loop B (see Fig. 2) is stable in dark and originates from a ferromagnetic phase formed under illumination in the LCMO ($x = 0.1$) film. No photoinduced effects were found in LCMO ($x = 0.3$) films having higher Ca doping.

IV. DISCUSSION

The results described above show that illumination with light having the photon energy in the range of 0.5–2.5 eV changes the magnetization and the microwave conductivity of LCMO ($x = 0.1$) films at low temperatures. A broad optical absorption band has been observed in this energy range in La based manganites,[17–19] where it was attributed to interionic electronic transitions between Jahn-Teller split e_g states of neighboring Mn^{3+} ions.[18] As a result a pair of Mn^{3+} ions disappears and Mn^{4+} and Mn^{2+} ions are formed according to the equation

$$Mn^{3+} + Mn^{3+} + h\nu \rightarrow Mn^{4+} + Mn^{2+}. \qquad (1)$$

Low doped LCMO compounds ($x < 0.15$) are FM insulators.[11] Referring to theoretical results,[7–9] we suppose that the increase of the microwave absorption below 60 K [see Fig. 1(b)] results from FM metallic droplets which are formed within the insulating phase. To describe the kinetics of the photoinduced transformation of the hysteresis loop shown in Fig. 3, we suggest that there are two types of the reaction described in Eq. (1). The first takes place between neighboring Mn^{3+} ions located in the insulating FM phase ($F1$). The second reaction takes place between neighboring Mn^{3+} ions located on the border between $F1$ and the metallic FM phase ($F2$). The Mn^{4+} ions generated by light on the border between the $F1$ and $F2$ phases will be involved in the metallic phase, leading to expansion of $F2$. The decrease of the number N_1 of the Mn^{3+} ions in the $F1$ phase can be expressed as

$$dn_1/dt = -I\sigma_1 n_1 n_1 - I\sigma_2 n_1 n_2, \qquad (2)$$

where $n_1 = N_1/N$ is the normalized number of the Mn^{3+} ions in $F1$, $n_2 = N_2/N$ is the normalized number of the Mn^{3+} ions in $F2$ but localized on the border with the $F1$ phase, N is the total concentration of the Mn atoms in the sample, I is the light intensity, and σ_1 and σ_2 are the cross sections of the photoinduced transitions. The increase of the number of the Mn ions involved in the $F2$ phase can be described by the equation

$$dn_2/dt = I\sigma_1 n_1 n_2. \qquad (3)$$

For simplicity we do not take above into account relaxation processes and other possible optical transitions which do not change the shape of the time dependencies of n_1 and n_2. The solution of the system of Eqs. (2) and (3) is shown by the thick solid lines in Fig. 6. In the same figure the normalized experimental dependencies of the M and C signals, the same as in Fig. 4, are plotted.

The time dependence for the M signal is well described by the function $n_2(t)$. Within the considered model the photo-
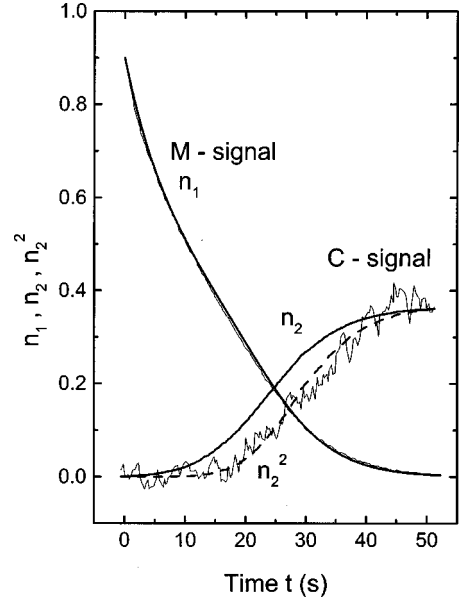

FIG. 6. Calculated dependencies of n_1 and n_2 (thick solid lines) and n_2^2 (dashed line) on the time t. The normalized experimental time dependencies of the M and C signals observed at $\lambda = 1.2\ \mu m$ are shown by the thin solid lines.

induced decrease of the number of the Mn^{3+} ions in the phase $F1$ is equivalent to the increase of the Mn^{4+} and Mn^{2+} ions in the sample. It is likely that the increase of the number of these paramagnetic ions is responsible for the photoinduced change of the M signal. The best fit for the M signal for $\lambda = 1.2\ \mu m$ is obtained at the following initial conditions: $n_1(0) = 0.9$ which corresponds to the doping level $x = 0.1$, $n_2(0) = 0.001$, $I\sigma_1 = 0.08$, and $I\sigma_2 = 0.44$. These parameters are physically reasonable. The number $n_2(0)$ corresponds to the small initial number of the Mn ions on the border between the $F1$ and $F2$ phases. From the values of $I\sigma_1 = 0.08$ and $I\sigma_2 = 0.44$ and the measured light intensity $I \approx 3.5 \times 10^{14}$ photons/cm^2s at $\lambda = 1.2\ \mu m$ the cross sections σ_1 and σ_2 can be determined as $\sigma_1 \approx 2.3 \times 10^{-16}\ cm^2$ and $\sigma_2 \approx 1.26 \times 10^{-15}\ cm^2$.

To describe the increase of the C signal with increasing t_R it must be taken into account that this signal corresponds to the increase of the microwave photoconductivity of the growing $F2$ phase and is therefore proportional to the volume of that phase. If we suppose that the part of the film in the $F2$ phase is a cylinder with radius R and height h, the C signal should be proportional to the volume of the cylinder, $C \sim \pi R^2 h$, whereas the number of the Mn ions on the border between the phases $F1$ and $F2$, n_2, should be proportional to its surface area $2\pi R h$. Consequently, the amplitude of the C signal should be proportional to n_2^2. The curve of n_2^2, normalized to the experimental value at $t = 52$ s, is shown by the dashed line in Fig. 6. A good agreement between the calculated values of $n_2(t)^2$ and the observed C signal is obtained using the same parameters as for fitting the data of the M signal.

V. SUMMARY

Photoinduced changes of the magnetic hysteresis and the microwave photoconductivity are observed in low doped

La$_{1-x}$Ca$_x$MnO$_3$ ($x=0.1$) films. These effects are detected in low magnetic fields and $T<60$ K under optical excitation in a broad range of wavelengths $\lambda=0.5-2.5~\mu$m. The amplitude of the hysteresis can be saturated at a low light intensity I, but the saturated value does not depend on I or λ. Instead, the time required for completion of the photoinduced transformation depends strongly on these parameters, showing a complex nonexponential time dependence. The kinetics of the photoinduced magnetization and the microwave photoconductivity can be well described by assuming the presence of small FM metallic regions within the insulating FM phase, as predicted theoretically for the low doped LCMO films.[7–9] These metallic areas are expanded by optically induced charge transfer between the Jahn-Teller split e_g states of neighboring Mn^{3+} ions.

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